

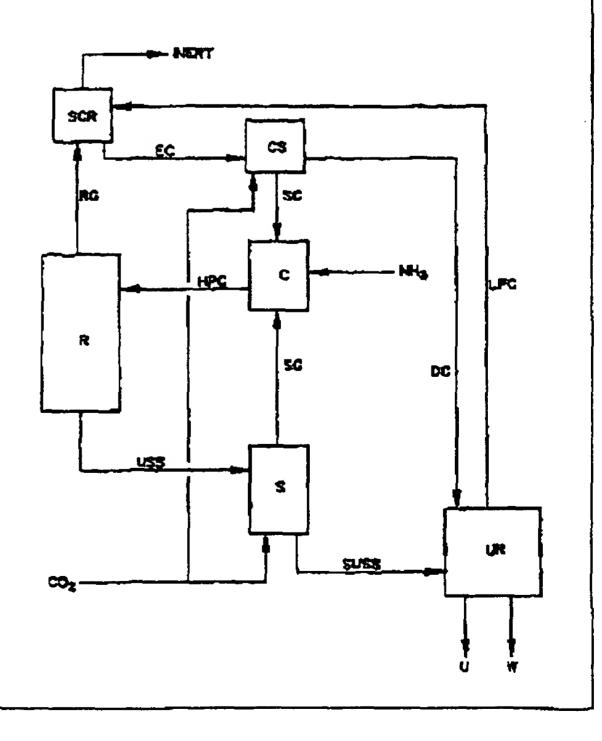
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6:		(11) International Publication Number:	WO 99/29663	
C07C 273/04	A1	(43) International Publication Date:	17 June 1999 (17.06.99)	
(21) International Application Number: PCT/NL	.98/006		• • • • • •	
(22) International Filing Date: 30 November 1998 (	<b>30.</b> 11.9	CZ, EE, GD, GE, HR, HU, U), I SI, LT, LV, MG, MK, MN, M SI, SK, SL, TR, TT, UA, US, U	IX, NO, NZ, TL, RO, SG	
		(GH, GM, KB, LS, MW, SD, SZ	•	
(30) Priority Data:		(AM, AZ, BY, KG, KZ, MD, RE		
1007713 5 December 1997 (05.12.97	) 1	IL (AT, BE, CH, CY, DIL DK, ES		
		LU, MC, NL, PT, SE), OAPI pa CM, GA, UN, UW, ML, MR, N		
(71) Applicant (for all designated States except US): D [NI/NI.]; Het Overloon 1, NL-6411 TB Heerlen			2, gr., 10, 10j.	
	. ,	Published		
(72) Inventor; and		With international rearch report.		
(75) Inventor/Applicant (for US only): MINNEN, Johann ricus [NL/NL]; Zwartveldsingel 3, NL-6088 19 (NL).		•		
(74) Agent: VAN BOKIKOVEN, Petrus, Hubertus, Ma troolbureau DSM, P.O. Box 9, NL-6160 MA Gele		•		
	<b></b> (11)	<b>7</b>		

## (54) Title: PROCESS FOR THE PREPARATION OF UREA

#### (57) Abstract

The invention relates to a process for the preparation of usea from armonia and carbon dioxide in which the low-pressure carbamate stream formed in the further upgrating of the usea synthesis solution is stripped in a CO2-carbamate stripper in countercurrent contact with CO2, which results in the formation of a gas mixture consisting substantially of ammonia and carbon dioxide. This gas mixture is preferably subsequently condensed in a high-pressure carbamate condenser and then returned to the synthesis zone.



### PROCESS FOR THE PREPARATION OF UREA

5

The invention relates to a process for the preparation of urea from ammonia and carbon dioxide.

Urea can be prepared by introducing ammonia and carbon dioxide into a synthesis zone at a suitable pressure (for example 12-40 MPa) and a suitable temperature (for example 160-250°C), which first results in the formation of ammonium carbamate according to the reaction:

 $2 NH_3 + CO_2 \rightarrow H_2N - CO - ONH_4$ 

Dehydration then causes the ammonium carbamate formed to form urea according to the equilibrium reaction:

20

 $H_2N-CO-ONH_4 \leftrightarrow H_2N-CO-NH_2 + H_2O$ 

The degree to which this last conversion proceeds depends on, among other factors, the temperature and the ammonia excess used. As the reaction product a solution is obtained that consists substantially of urea, water, ammonium carbamate and unbound ammonia. The ammonium carbamate and the ammonia must be removed from the solution and are preferably returned to the synthesis zone. In addition to the aforementioned solution, a gas mixture is formed in the synthesis zone, which consists of non-converted ammonia and carbon dioxide plus inert gases. Ammonia and carbon dioxide are removed from this gas mixture and are preferably also returned to the synthesis zone. The synthesis zone may comprise separate zones for the

. 30

formation of ammonium carbamate and urea. These zones may however also be united in a single apparatus.

In practice, different methods are used for the preparation of urea. At first urea was prepared in so-called conventional high-pressure urea plants, which were at the end of the 1960s however succeeded by processes carried out in so-called urea stripping plants.

A conventional high-pressure urea plant is 10 understood to be a urea plant in which the decomposition of the ammonium carbamate not converted into urea and the expulsion of the usual ammonia excess take place at a substantially lower pressure than the pressure in the synthesis reactor itself. In a 15 conventional high-pressure urea plant the synthesis reactor is usually operated at a temperature of 180-250°C and a pressure of 15-40 MPa. In a conventional high-pressure urea plant the reactants not converted into urea are, after expansion, dissociation and 20 condensation at a pressure of between 1.5 and 10 Mpa, returned to the urea synthesis as a carbamate stream. In addition, in a conventional high-pressure urea plant ammonia and carbon dioxide are fed directly to the urea reactor. The molar  $NH_3/CO_2$  ratio (= N/C ratio) in the urea synthesis lies between 3 and 5 in a conventional high-pressure urea process.

These conventional urea plants were initially designed as so-called once-through processes, in which the non-converted ammonia was neutralized with acid (for example nitric acid) and converted into ammonium salts (for example ammonium nitrate). Major disadvantages of this process were this large amount of ammonium salt and the low degree of CO<sub>2</sub> conversion.

These conventional once-through urea processes were soon replaced by the so-called conventional recycle processes, in which all the non-converted ammonia and carbon dioxide are returned to the urea reactor. This recycling is carried out in two steps. A first recycling step at a medium pressure (1.8-2.5 MPa) and a second recycling step at a low pressure (0.2-0.5 MPa). In the first recycling step the urea synthesis solution coming from the reactor is heated in a heater, upon 10 which ammonium carbamate decomposes into gaseous ammonia and carbon dioxide while further the excess ammonia also evaporates here. This gas mixture is subsequently converted into pure ammonia and a watercontaining ammonium carbamate stream in a rectifying column. Both streams are returned to the urea reactor. 15 In the second recycling step the urea solution from the first recycling step is reheated and then separated. The gas stream thus obtained is condensed and subsequently fed to the rectifying column of the first step. Next, urea is released from the urea solution 20 coming from the second recycling step, in the evaporation at reduced pressure, through the evaporation of water. The two recycling steps and the evaporation together constitute the main part of the urea recovery. 25

A urea stripping plant is understood to be a urea plant in which the greater parts of the decomposition of the ammonium carbamate not converted into urea and the expulsion of the usual ammonia excess take place at a pressure that is essentially almost the same as the pressure in the synthesis reactor. This decomposition/expulsion takes place in a stripper, whether or not with the addition of a stripping medium.

. 30

In a stripping process, carbon dioxide and/or ammonia can be used as stripping gas before these before and a stripping gas before these before and a stripping gas before these before the second the Car we used to the reactor. This stripping takes place in all dosed to the reactor. MO 38153663 a stripper placed downstream of the reactor, solution coming from the urea reactor, which, addition to urea, and maken diamate and water, and addition to urea, and analyse analyse and analyse analyse and analyse analyse analyse and analyse analyse analyse analyse and analyse analyse analyse analyse and analyse a contains ammonia and carbon dioxide, being stripped, Contains amount and Gas With the supply of heat. It is with the supply of heat. Stripping means and amnorthm carbanate is decomposed and the ammonia and carbon dioxide present are the amonia and the From the urea solution exclusively by means of the SUPPLY OF heat. The gas stream containing ammonia and supply of heat. The same is not assessed to the same is not as a same is not assessed to the same is not as a same is not assessed to the same is not assessed to the same is not as a same is not a carbon dioxide that is released from the stripper is cardul charte reactor via a high-pressure carbanate returned to the reactor via a The gas mixture that has not reacted in the Urea synthesis is removed from the synthesis section. Via a blow-down stream. In addition to the condensable annonia and carbon dioxide, this gas minh and and carbon dioxide, as an analysis and c off-gae) also contains inert gases such as, example:

also concarns and optionally hydrogen. condenser. These inert gases derive from the raw materials and THEE THE MAKE UP SIT IN the Carbon dioxide feed to me. ETOM the make-up all in the materials from corrosion.

Synthesis to protect the materials and the state of th gas stream is blown of the reason of the synthesis section. EXAMPLE downstream of the reactor or downstream of the high-name and a second or the symple downstream of the reactor or downstream of the reactor of the second of the se example converted to the condensation depending on the high-pressure carbanate condensation. Process route chosen. It is however preferable to absorb the condensable components (ammonia and carbon dioxide) in a high-pressure scrubber at synthesis Preseure before the inerthan was annian annian and annian Brenence reform actions the condensable components, and high-pressure actioner the condensable components. 25

- 5 -

ammonia and carbon dioxide, are absorbed from the synthesis off-gas into the low-pressure carbamate stream formed in the further upgrading. This scrubbing process in the high-pressure scrubber can be stimulated by using a heat exchanger that extracts heat from the process. The carbamate stream from the high-pressure scrubber, which contains the ammonia and carbon dioxide absorbed from the synthesis off-gas, is returned to the synthesis via the high-pressure carbamate condenser. The reactor, high-pressure scrubber, stripper and highpressure carbamate condenser are the most important parts of the high-pressure section of a urea stripping plant.

In a urea stripping plant the synthesis reactor is operated at a temperature of 160-240°C and 15 preferably at a temperature of 170-220°C. The pressure in the synthesis reactor is 12-21 MPA, preferably 12.5-19 MPa. The N/C ratio in the synthesis in a stripping plant lies between 2.5 and 4. The synthesis can be carried out in one or two reactors. When use is made of 20 two reactors, the first reactor can be operated using virtually fresh raw materials and the second using raw materials entirely or partly recycled, for example from the urea recovery.

A frequently used embodiment for the preparation of urea according to a stripping process is the Stamicarbon CO2-stripping process described in Buropean Chemical News, Urea Supplement, of 17 January 1969, pages 17-20. In this process the urea synthesis solution formed in the synthesis zone at a high pressure and temperature is subjected to a stripping treatment at synthesis pressure by bringing the solution into countercurrent contact with gaseous

25

30

carbon dioxide while heat is being supplied. This causes the greater part of the ammonium carbamate present in the solution to be decomposed into ammonia and carbon dioxide. These decomposition products are expelled from the solution in gaseous form and are discharged together with a small amount of water vapour and the carbon dioxide used for the stripping. Besides with the aid of carbon dioxide, as described in this publication, such a stripping treatment can also be 10 carried out thermally or using gaseous ammonia as the stripping gas, or using a mixture of the aforementioned gases. The greater part of the gas mixture obtained in the stripping treatment is condensed and adsorbed in a high-pressure carbamate condenser, after which the 15 ammonium carbamate formed is returned to the synthesis zone for the formation of urea. The stripping of the urea synthesis solution with a stripping medium can take place in more than one stripper.

The high-pressure carbamate condenser can for example be designed as a so-called submerged 20 condenser as described in NL-A-8400839. The gas mixture to be condensed is then introduced into the shell-side space of a shell-and-tube heat exchanger, into which space a diluted carbamate solution coming from the high-pressure scrubber is also introduced. The heat of dissolution and condensation then released is discharged with the aid of a medium flowing through tubes, for example water, which is in the process converted into low-pressure steam. The submerged condenser can be placed horizontally or vertically. It . 30 is however particularly advantageous to carry out the condensation in a horizontally placed submerged condenser (a so-called pool condenser; see for example

Nitrogen No 222, July-August 1996, pp. 29-31), because, in comparison with other embodiments of this condenser, the liquid generally has a longer residence time in the pool condenser. This results in the formation of extra urea, which raises the boiling point, so that the difference in temperature between the carbamate solution containing urea and the cooling medium increases, resulting in better heat transfer.

After the stripping treatment, the pressure of the stripped urea synthesis solution is reduced in 10 the urea recovery and the solution is evaporated, after which urea is released. This urea recovery is carried out in one or more pressure steps, depending on the degree to which carbamate has already been expelled in the stripper(s). This produces a low-pressure carbamate 15 stream in the recovery. This low-pressure carbamate stream is returned via the high-pressure scrubber to the section operating at synthesis pressure. In the high-pressure scrubber this low-pressure carbamate stream scrubs non-converted ammonia and carbon dioxide from the gas mixture blown down from the section operating at synthesis pressure to remove the noncondensable gases from the synthesis section.

The theoretically feasible degree of conversion of ammonia and carbon dioxide into urea is determined by the thermodynamic position of the equilibrium and depends on for example the NH<sub>3</sub>/CO<sub>2</sub> ratio, the H<sub>2</sub>O/CO<sub>2</sub> ratio and the temperature and can be calculated using the models for example described in Bull. of the Chem. Soc. of Japan 1972, vol. 45, pp. 1339-1345, and J. Applied Chem. of the USSR (1981), vol. 54, pp. 1898-1901.

- 8 -

The conversion of ammonium carbamate into urea and water in the reactor can be effected by ensuring a sufficiently long residence time of the reaction mixture in the reactor. The residence time will generally be more than 10 min., preferably more than 20 min. The residence time will generally be shorter than 2 hours, preferably shorter than 1 hour. Preferably the residence time of the urea synthesis solution in the reactor is chosen so that at least 90% of the theoretically feasible amount of urea is prepared, in particular more than 95%. At a higher temperature and pressure in the reactor a shorter residence time is often sufficient for obtaining a high degree of conversion.

The conversion of ammonium carbamate into urea is an equilibrium reaction whose position is adversely influenced by the water present in the reactor.

15

· An important source of water is the lowpressure carbamate stream which is formed during the 20 further upgrading of the urea synthesis solution and which is fed to the synthesis zone via the highpressure scrubber in a CO2 stripping plant as described above. In a conventional urea plant this low-pressure carbamate stream can be fed directly to the reactor. This carbamate stream has a high water content and is disadvantageous for the conversion of ammonia and carbon dioxide into urea. This carbamate stream is, however, an important source of raw materials, which is why recycling of this carbamate stream to the synthesis .30 zone is nevertheless opted for in urea plants. A further disadvantage of this carbamate stream with its high water content is its corrosive character at a high

25

. 30

temperature. This imposes high demands on the quality of all the pipes and equipment operating at synthesis pressure.

The degree of CO<sub>2</sub> conversion is used as a measure of the degree of conversion of ammonia and carbon dioxide into urea. In urea stripping plants this degree usually lies between 58 and 62% and in conventional urea plants between 64 and 68%.

found that the degree of CO<sub>2</sub> conversion can be substantially increased by stripping the low-pressure carbamate stream formed during the further upgrading of the urea synthesis solution in countercurrent contact with CO<sub>2</sub> in a CO<sub>2</sub> carbamate stripper, which results in a gas mixture consisting substantially of ammonia and carbon dioxide.

This gas mixture is preferably subsequently condensed in a high-pressure carbamate condenser and then returned to the synthesis zone.

In a urea stripping plant the condensation of carbamate can preferably take place in the high-pressure carbamate condenser already present. In a conventional urea plant the gas mixture formed is returned from the CO<sub>2</sub>-carbamate stripper to the synthesis, but is preferably condensed in a high-pressure carbamate condenser to be additionally installed, after which it is returned to the synthesis.

It is also preferable to supply the ammonia feed to this high-pressure carbamate condenser and transfer it to the synthesis together with the carbamate stream. In both the conventional urea plants and the urea stripping plants low-pressure steam is produced in this high-pressure carbamate condenser,

. 30

which can be used in the downstream processing. The advantage of this is that the steam consumption in a conventional urea plant decreases substantially.

In addition to the gas mixture, consisting substantially of ammonia and carbon dioxide, a liquid phase with a high water content is formed in the CO<sub>2</sub>-carbamate stripper. The reactants ammonia, ammonium carbamate and carbon dioxide can be removed from this liquid phase with a high water content for example through a reduction in pressure and further purification by means of steam stripping in for example the urea recovery.

The separation of the low-pressure ammonium carbamate stream into a gas phase and a liquid phase with a high water content is also described in WO 96/23767 and EP-A-727414. In these publications the separation is however not effected in an additionally installed carbamate stripper in which the low-pressure ammonium carbamate stream is stripped with the aid of carbon dioxide, but by supplying heat. The advantage of stripping with CO2 in an additionally installed CO2carbamate stripper is that, because of the stripping with CO2. during the separation of the low-pressure carbamate stream into a gas phase and a liquid phase with a high water content, the process conditions are much milder than in the separation through the supply of heat as used in the aforementioned publications. These much milder conditions are advantageous in selecting materials in connection with corrosion. Cheaper types of steel can then be used. Feeding the low-pressure carbamate stream to the existing stripper in a urea stripping plant presents the drawback that no use is made of the smaller amount of urea synthesis

solution that has to be stripped and hence no saving in high-pressure steam is achieved.

Any type of stripper can be used as the CO2carbamate stripper. Preferably use is made of a stripper based on the countercurrent principle. In particular use is made of a stripper of the same type as the CO2 stripper in the aforementioned Stamicarbon CO2-stripping process. The pressure in the CO2 carbamate stripper is virtually identical to the pressure in the urea synthesis. In conventional urea plants the pressure in the CO2-carbamate stripper may preferably vary between 15 and 40 MPa. In urea stripping plants the pressure may preferably vary between 12.5 and 19 MPa. In both a conventional urea plant and a urea stripping plant the temperature at the 15 top of the CO2-carbamate stripper usually lies below 270 °C, preferably below 240°C. The temperature usually lies above 120°C, in particular above 150°C. The residence time of the low-pressure carbamate stream in the CO2carbamate stripper is short, being less than 10 minutes, in particular less than 5 minutes.

Using an additional CO2-carbamate stripper means that use is made of the absorbing capacity of the low-pressure carbamate stream from the urea recovery in the high-pressure scrubber of a urea stripping plant, while it is simultaneously ensured that no excess water is fed to the synthesis section. This ensures that, in the scrubber, ammonia and carbon dioxide are removed from the gas mixture to be blown down from the synthesis section (containing the non-condensable components). The use of the low-pressure carbamate stream presents the advantage that the absorption in the high-pressure scrubber is optimal because of this

20

25

. 30

- 12 -

carbamate stream's low vapour pressure. This carbamate stream has a vapour pressure that corresponds to the vapour pressure of the urea recovery and lies between 0.2 and 2.5 Mpa, which is much lower than the synthesis pressure, which lies between 12.5 and 19 MPa. In this process an inert stream is moreover obtained from the high-pressure scrubber, which contains fewer traces of ammonia and carbon dioxide, as a result of which the further off-gas purification that is often necessary in view of environmental requirements will cost less.

A second advantage in a urea stripping plant is that better absorption takes place in the high-pressure scrubber of a stripping plant, as a result of which the inerts content in the reactor off-gas can be reduced. This enables a higher temperature at the same pressure in the synthesis zone, as a result of which the yield becomes higher and less energy is consumed. It is also possible to operate the reactor at the same temperature but at a lower pressure, and this also presents an energy advantage in bringing the ammonia and carbon dioxide to the required pressure.

15

20

25

carbamate stripper contains only little ammonia and carbon dioxide. This water stream can be returned to the urea recovery, where these components are removed from the water stream via a desorption step and are added to the low-pressure carbamate stream after condensation in a condenser. The water stream from the CO<sub>2</sub>-carbamate stripper can be given some residence time under synthesis conditions before it is returned to the recovery. The result is that still some urea formation takes place at the prevailing synthesis pressure and the corresponding temperature. This water is then

transferred to the recovery, where this urea is It has been found that a degree of coa MO 33[53663 conversion of more than 70% is achieved in urea Btripping plants with the process according to in the urea plant's capacity. In conventional urea Plants, recovered. Plants, the equilibrium is achieved with the present invention. With carbon dioxide it is possible to avoid the need to WILL CALDUL CLOXIUE LE LA PUSALULE LO AVOIO LUE REEU L'A PUSALULE LO AVOIO L'ARE REEU L'A PUSALULE LO AVOIO L'ARE REEU L'A PUSALULE L'O AVOIO L'ARE REEU L'A PUSALULE LO AVOIO L'ARE REEU L'A PUSALULE L'O AVOIO L'ARE REEU L'A PUSALULE L'ARE REEU L'A PUSALULE L'ARE REEU L'A PUSALULE L'ARE REEU L'ARE as would be the case if the separation into Stream and a liquid stream with a high water hear Were to be effected exclusively by supplying heat.

When the shear that common or around the supplying heat. PIEBERTS the advantage that Collogion Problems due to the aggressiveness of anmonium carbamate at high 10 It has furthermore been found that this Process is very suitable for improving and optimizing existing urea plants. This invention leads to a temperatures are avoided. existing uses plants. Luke 20% in the load on the reduction of approximately 20% in the near and a serious reduction of approximately 20% in the load on the reduction of approximately 20% in the load on the reduction of approximately 20% in the load on the reduction of approximately 20% in the load on the reduction of approximately 20% in the load on the reduction of approximately 20% in the load on the reduction of approximately 20% in the load on the reduction of approximately 20% in the load on the reduction of approximately 20% in the load on the reduction of approximately 20% in the load on the reduction of approximately 20% in the load on the reduction of approximately 20% in the load on the reduction of approximately 20% in the load on the reduction of approximately 20% in the load on the load of the load on the load on the load on the load of the load on the load of the loa requerion of approximate the high-pressure carbanate condenser and the subsequent recovery section(s) in urea stripping plants. The load on the recovery Substantially decreased as a result of this invention. sections of conventional urea plants is also Both conventional urea plants and urea and with warm 20 Can be debottlenecked at only low costs and with very good results by additionally installing a Cor-carbanate The invention bence also relates to a method for improving and optimizing an existing urea 25 stripper. 30

stripping plant with a high-pressure scrubber. This can be effected by installing a CO2-carbamate stripper between the high-pressure scrubber and the highpressure carbamate condenser. The invention further 5 relates to a method for improving and optimizing a urea plant without a high-pressure scrubber. This can be effected by installing a CO2-carbamate stripper directly after the urea recovery for stripping of the lowpressure ammonium carbamate stream with CO2. It is in 10 these processes however preferable to additionally install a high-pressure scrubber at the point where the inerts-containing synthesis off-gas stream leaves the synthesis section, and to use the low-pressure carbamate stream as a scrubbing liquid in it. The 15 carbamate stream coming from the high-pressure scrubber can then be fed to the CO2-carbamate stripper. This carbamate stream is stripped in the CO2-carbamate stripper, after which the carbamate gases that are virtually free of water are fed directly, or preferably via a high-pressure carbamate condenser, to the synthesis section.

The invention also relates to a method for improving and optimizing conventional urea plants. This can be effected by installing a CO<sub>1</sub>-carbamate stripper directly after the urea recovery, after which the gas stream from the CO<sub>2</sub>-carbamate stripper is condensed in an additionally installed high-pressure carbamate condenser.

The invention further relates to a second 30 method for improving and optimizing an existing conventional urea plant. This can be effected by additionally installing a high-pressure scrubber, a CO<sub>2</sub>- carbamate stripper and a high-pressure carbamate condenser.

The invention is hence suitable for use in all existing urea processes, both conventional urea processes and urea stripping processes.

Examples of conventional urea processes in which the invention can be used are:

- 16 -

- Urea Technologies Inc. (UTI); Heat Recycle Process (HRP);
- Mitsui Toatsu Corporation; Conventional Process of Toyo Engineering Corporation;
- 5 Vulcan; Once-Through Urea Process.

Examples of urea stripping processes in which the invention can be used are:

- 10 Stamicarbon; CO2-Stripping Process;
  - Snamprogetti; Ammonia-Stripping Process;
  - Snamprogetti; Self-stripping Process;
  - Toyo Engineering Corporation; ACES Process
    (Advanced process for Cost and Energy Saving);
- 15 Montedison; Isobaric-Double-Recycle (IDR) process;
  - Urea Casale SA; HEC process.

. 30

Of the urea processes mentioned above the urea stripping processes of Stamicarbon, Toyo-ACES and IDR have a high-pressure scrubber. In this high-pressure scrubber the synthesis off-gas from the reactor is incorporated in the low-pressure carbamate stream coming from the urea recovery. In these processes the CO<sub>2</sub>-carbamate stripper is preferably installed directly after the high-pressure scrubber.

In urea processes without a high-pressure scrubber, such as the Snamprogetti, UTI and Urea Casale processes, the CO<sub>2</sub>-carbamate stripper is installed directly after the urea recovery. In these processes it is however preferable, as already indicated above, to additionally install a high-pressure scrubber at the point where the inerts-containing synthesis off-gas stream leaves the synthesis section, and to use the

15

20

low-pressure carbamate stream as a scrubbing liquid in it. The carbamate stream leaving the high-pressure scrubber can then be fed to the CO<sub>2</sub>-carbamate stripper. In the CO<sub>2</sub>-carbamate stripper this carbamate stream is then stripped with CO<sub>2</sub>, after which the carbamate off-gases which are virtually free of water are fed directly, or preferably via the high-pressure carbamate condenser, to the synthesis section. The water stream from the CO<sub>2</sub>-carbamate stripper can be returned to the urea recovery.

The invention will be further elucidated below by way of illustration with reference to the following figures, of which Figures 1 and 5 represent the state of the art and Figures 2,3,4,6,7 and 8 are embodiments of the present invention.

- Figure 1: Part of a conventional urea plant without a CO<sub>2</sub>-carbamate stripper
- Figure 2: Part of a conventional urea plant with a CO<sub>2</sub>carbamate stripper and a high-pressure
  carbamate condenser
- Figure 3: Part of a conventional urea plant with a CO<sub>2</sub>-carbamate stripper, high-pressure carbamate condenser and high-pressure scrubber
- Figure 4: Part of a conventional urea plant according to the UTI process with a CO<sub>2</sub>-carbamate stripper
  - Figure 5: Part of a urea stripping plant according to the Stamicarbon CO<sub>2</sub>-stripping process without a CO<sub>2</sub>-carbamate stripper
- 30 Figure 6: Part of a urea stripping plant according to the Stamicarbon CO<sub>2</sub>-stripping process with a CO<sub>2</sub>-carbamate stripper

- 18 -

Figure 7: Part of a urea stripping plant according to the TEC-ACES process with a CO2-carbamate stripper

Figure 8: Part of a urea plant according to the Snamprogetti self-stripping process with a CO<sub>3</sub>-carbamate stripper and a high-pressure scrubber.

5

In these figures the same symbols are used for corresponding parts and corresponding streams. Figures 2,3,4,6,7 and 8 present the various preferred embodiments by way of illustration. Other embodiments in which the ammonium carbamate stream of reduced pressure is stripped with carbon dioxide in an additional CO<sub>2</sub>-carbamate stripper are also possible.

In Figure 1 R represents a urea reactor in a conventional urea plant, to which ammonia and carbon dioxide are supplied. From the reactor comes the urea synthesis solution (USS), which is fed to the urea recovery (UR). In the UR urea (U) is released and a water stream (W) and a low-pressure ammonium carbamate stream (LPC) are formed. This LPC is returned to the reactor.

Figure 2 represents an embodiment of the invention used
in a conventional urea plant. R represents the urea
reactor to which a portion of the carbon dioxide is
supplied. The urea synthesis solution (USS) is
transferred to the urea recovery (UR), where urea (U)
is released and water (W) is discharged. The lowpressure ammonium carbamate stream (LPC) formed in the
UR is fed to a CO<sub>2</sub>-carbamate stripper (CS), in which the
LPC is stripped with carbon dioxide. The stripped LPC
is fed to the reactor as a gas mixture consisting

substantially of ammonia and carbon dioxide (SC) together with the anmonia feed via a high-pressure carbanate condenser. The diluted aqueous carbanate Carpanate Concenser. The CS is recycled to the Urea solution (DC) formed in the CS is recycled to the Urea MO del Lideres recovery schematically represents the conventional urea Figure of Figure 2 in which a high pressure scrubber (SCR) has been additionally installed. Here the Synthesis off-gas from the reaction section (RG) incorporated in the low-pressure ammonium carbamate Incorporated in the urea recovery (UR). The enriched stream (LPC) from the urea for form the property (UR). Stream (LIPE) ITOM the Listed from the high-pressure carbanate stream (EC) Carpanare Buream (EC) La red from the dign-pressure it is scrubber to the Cor-carbamate stripper (CS); where it is scrubber to the cor-carbamate stripper (CS); Figure 4 schematically represents one possible way of conventional urea plant according to the UTI process. installing a co2-carbamate stripper (cs) in a The CS has been installed between the urea recovery (IR) and the urea reactor (R). The urea synthesis EDIUTION (USS) is fed to the urea symmetry (UR);

Solution (USS) is reactor in the urea symmetry (UR);

The urea symmetry (UR); EOLUCION (USS) IS red to the urea recovery ammonia and a urea (U) is released and where water (W); are ammonian carbanata erroam (1.00) are low-pressure ammonium carbamate stream (LPC) are formed. The LPC is stripped with carbon dioxide in the consisting substantially of ammonia and carbon above and according to the contract of the CS; after which the resulting gas stream (SC); is fed to the reactor. The aqueous carbamate stream In rigure 5 R represents a reactor in a small amount a second of the sec (DC) is recycled to the urea recovery (UR) Stripping plant in which carbon dioxide and ammonia are stripping plant in which was armoned a solution (see SCILPPING PLANC Urea. The Urea Synthesis Solution (USS) coming from the reactor is fed to a cos stripper, in coming from the reactor is red into a gas stream (sG) and a which the USS is converted into a gas stream (se) annaiore Wilch the Upp 18 converted late a gas stream (SG) consists
liquid stream (SUSS). The gas stream 25 30

substantially of ammonia and carbon dioxide and the SUSS is the stripped USS. The stream containing the stripped urea synthesis solution SUSS is transferred to the urea recovery (UR), where urea (U) is released and water (W) is discharged. In the UR a low-pressure ammonium carbamate stream (LPC) is obtained, which is fed to the high-pressure scrubber (SCR). In this scrubber the LPC is brought into contact with the gas stream coming from the reactor (RG) which consists substantially of ammonia and carbon dioxide but which 10 also contains the inert components (non-condensable components) present in the carbon dioxide feed and the ammonia feed. The enriched carbamate stream (EC) coming from the SCR is transferred to the high-pressure 15 carbamate condenser (C), in which the SG stream is condensed with the aid of EC. The resulting highpressure carbamate stream (HPC) is returned to the reactor. The fresh ammonia is in this example fed to the high-pressure carbamate condenser (C), but it can of course also be fed to a different point in the  $R \rightarrow S$  $\rightarrow$  C  $\rightarrow$  R loop or in the R  $\rightarrow$  SCR  $\rightarrow$  C  $\rightarrow$  R loop. Figure 6 schematically represents one possible way of incorporating an additional CO1-carbamate stripper (CS) in a Stamicarbon CO2-stripping plant. Here, a CS has been installed between the high-pressure scrubber (SCR) and the high-pressure carbamate condenser (C) in Figure 5. In the CS the low-pressure ammonium carbamate stream (LPC) is stripped with carbon dioxide, after which the gases released (SC) are transferred to the highpressure condenser (C). The carbamate stream with a 30 high water content (DC) is recycled from the CS to the urea recovery.

Figure 7 schematically represents a urea process according to the TEC-ACES process, in which, by way of illustration, a CO2-carbamate stripper has been installed between the high-pressure scrubber (SCR) and the high-pressure carbamate condenser (C). In this process the heat released in the high-pressure carbamate condenser (C) is used for direct heating of the urea synthesis solution (USS) treated in the stripper (S). The symbols in this figure represent parts of plants and streams as in Figure 5.

Figure 8 shows a urea process according to the Snamprogetti Self-Stripping process in which a high-pressure scrubber (SCR) and a CO2-carbamate stripper (SC) have additionally been included. The symbols again have the same meanings as in Figure 5.

The invention will be further elucidated with reference to the following examples:

# 20 Comparative Example A

Table 1 below indicates the compositions of the various streams in percent by weight for a Stamicarbon CO<sub>2</sub>-stripping plant as indicated in Figure 5. From the compositions of the streams a value of 58.5% follows for the degree of CO<sub>2</sub> conversion.

Table 1: Process streams in a Stamicarbon CO2-stripping plant

Stream	Urea	NH <sub>3</sub>	CO <sub>2</sub>	H <sub>2</sub> O	Inert
uss	33.9	30.2	17.7	18.2	ì
CO <sub>2</sub>	-	-	93.6	1.1	5.3
SUSS	55	7.8	10.2	27	-
SG	-	61.9	32.0	4.9	1.2
NH <sub>1</sub>	-	99.5	-	0.5	-
HPC	-	49.2	41.9	7.6	1.3
RG	-	68.6	21.0	4.4	6.0
EC	-	38.8	39.2	22.0	-
LPC	-	29.6	37.3	33.1	-
Inert	-	8.8	3.3	-	87.9

# Example I

various streams in percent by weight for a Stamicarbon CO<sub>2</sub>-stripping plant in which a CO<sub>2</sub>-carbamate stripper has additionally been installed as indicated in Figure 6. From the compositions of the streams a value of 70.0% follows for the degree of CO<sub>2</sub> conversion.

Table 2: Process streams in a Stamicarbon CO<sub>2</sub>-stripping plant with a CO<sub>2</sub>-carbamate stripper

Stream	Urea	NH <sub>3</sub>	CO <sup>3</sup>	H <sub>2</sub> O	Inert
USS	43.8	28.3	13.8	14.1	-
CO <sub>2</sub>	11-17	- 1	93.6	1.1	5.3
suss	62.4	8.8	11.5	17.3	-
SG	_	60.0	31.5	7.0	1.5
NH <sub>3</sub>	_	99.5	-	0.5	-
RPC	_	50.2	42.6	6.2	1.0
RG	-	68.7	20.9	4.4	6.0
BC	-	38.2	39.1	22.7	-
sc	-	52.5	27.7	19.5	0.5
LPC	-	29.6	37.3	33.1	-
DC	-	7.9	10.2	81.9	<b>-</b>
Inert	_	8.8	3.3	-	87.9

The  $CO_2$  stream to S is 81% and the  $CO_2$  stream to CS is 19% of the total feed.

The flows of the various streams in Example I clearly differ from the flows of the corresponding streams in Comparative Example A. Table 3 below indicates the ratios of the flows of Example I and the flows of Comparative Example A.

Table 3: Ratios of the flows in Example I and Example A

Stream	Ratio of the flows in Example I and Example A
uss	0.78
suss	0.90
sG	0.70
HPC	0.83
EC	1.06
LBC	1.10

- 25 -

## CLAIMS

- 1. Process for the preparation of urea from ammonia and carbon dioxide, characterized in that the low-pressure carbamate stream formed during the further upgrading of the urea synthesis solution is stripped in a CO<sub>2</sub>-carbamate stripper in countercurrent contact with CO<sub>2</sub>, which results in a gas mixture consisting substantially of ammonia and carbon dioxide.
  - 2. process according to Claim 1, characterized in that this gas mixture is condensed in a highpressure carbamate condenser and is then returned to the synthesis zone.
- 15 3. Process according to Claim 1 or Claim 2, characterized in that, in a urea stripping plant, the condensation of carbamate takes place in the high-pressure carbamate condenser already present.
- 4. Process according to Claim 1 or Claim 2,

  characterized in that, in a conventional urea

  plant, the gas mixture formed from the CO<sub>2</sub>
  carbamate stripper is condensed in a high-pressure

  carbamate condenser to be additionally installed

  and is then returned to the synthesis.
- 25 5. Process according to any one of Claims 1-4, characterized in that a stripper that operates according to the countercurrent principle is used as the CO2-carbamate stripper.
- 6. Process according to Claim 5, characterized in that use is made of a CO<sub>2</sub>-carbamate stripper of the same type as the CO<sub>2</sub> stripper in the aforementioned Stamicarbon CO<sub>2</sub>-stripping process.

- 26 -

- 7. Process according to Claim 5, characterized in that the pressure in the CO<sub>2</sub>-carbamate stripper, used in a conventional urea plant, is between 15 and 40 MPa.
- 5 8. Process according to Claim 5, characterized in that the pressure in the CO<sub>2</sub>-carbamate stripper, used in a urea stripping plant, is between 12.5 and 19 MPa.
- 9. Process according to Claim 4, characterized in
  that a high-pressure scrubber is additionally
  installed at the point where the inerts-containing
  synthesis off-gas stream leaves the synthesis
  section and using the low-pressure carbamate
  stream as a scrubbing liquid in it, after which
  the carbamate stream coming from the high-pressure
  scrubber is fed to the CO<sub>2</sub>-carbamate stripper.
  - 10. Method for improving and optimizing an existing urea stripping plant with a high-pressure scrubber by installing a CO2-carbamate stripper between the high-pressure scrubber and the high-pressure carbamate condenser.

20

25

- 11. Method for improving and optimizing a urea plant without a high-pressure scrubber by installing a CO<sub>2</sub>-carbamate stripper directly after the urea recovery for stripping with CO<sub>2</sub> of the low-pressure ammonium carbamate stream.
- 12. Method for improving and optimizing a urea plant without a high-pressure scrubber by installing a CO<sub>2</sub>-carbamate stripper directly after the urea recovery for stripping with CO<sub>2</sub> of the low-pressure ammonium carbamate stream, a high-pressure scrubber having been additionally installed at the point where the inerts-containing synthesis off-

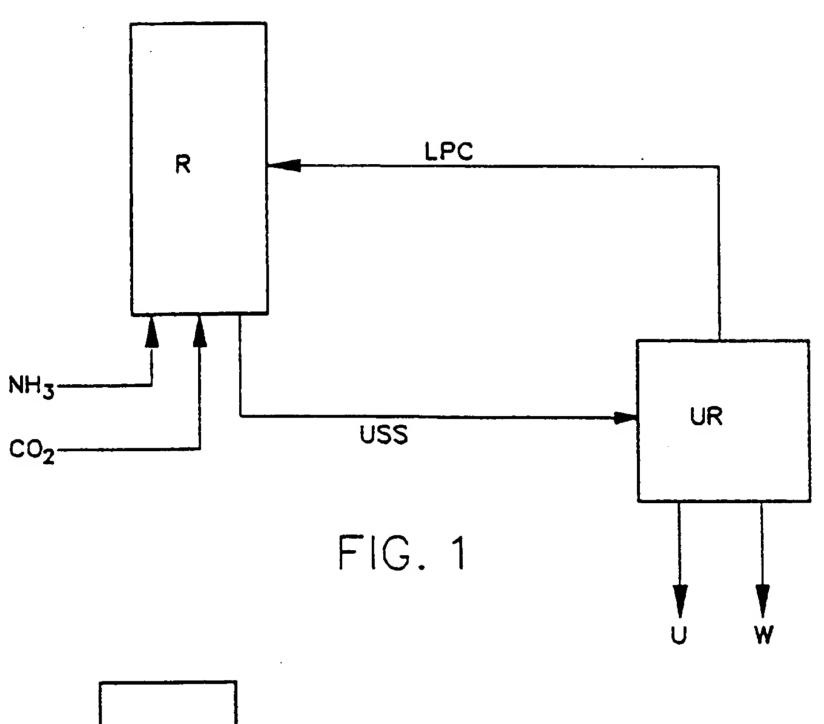
10

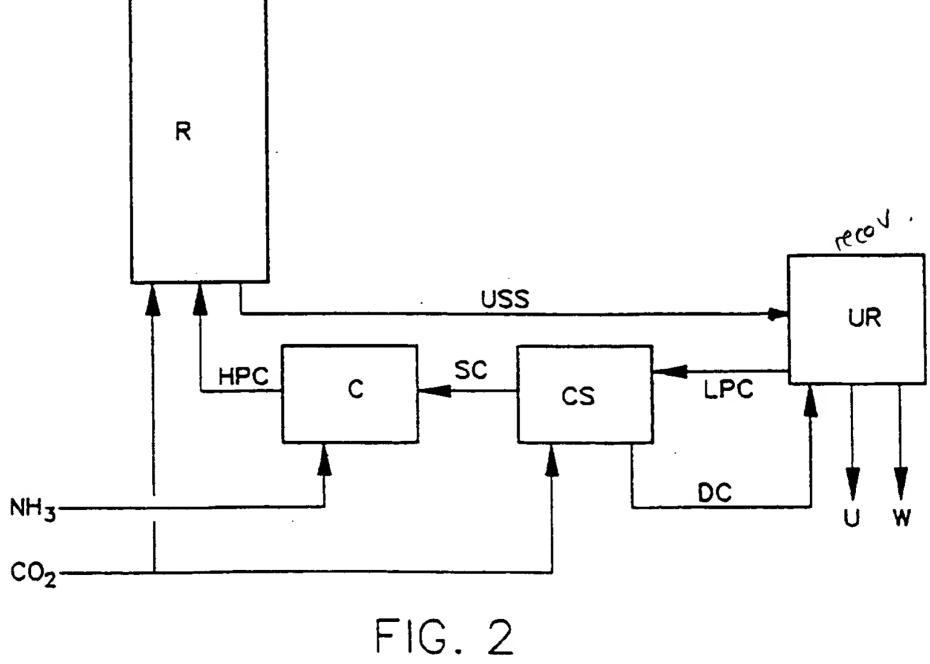
15

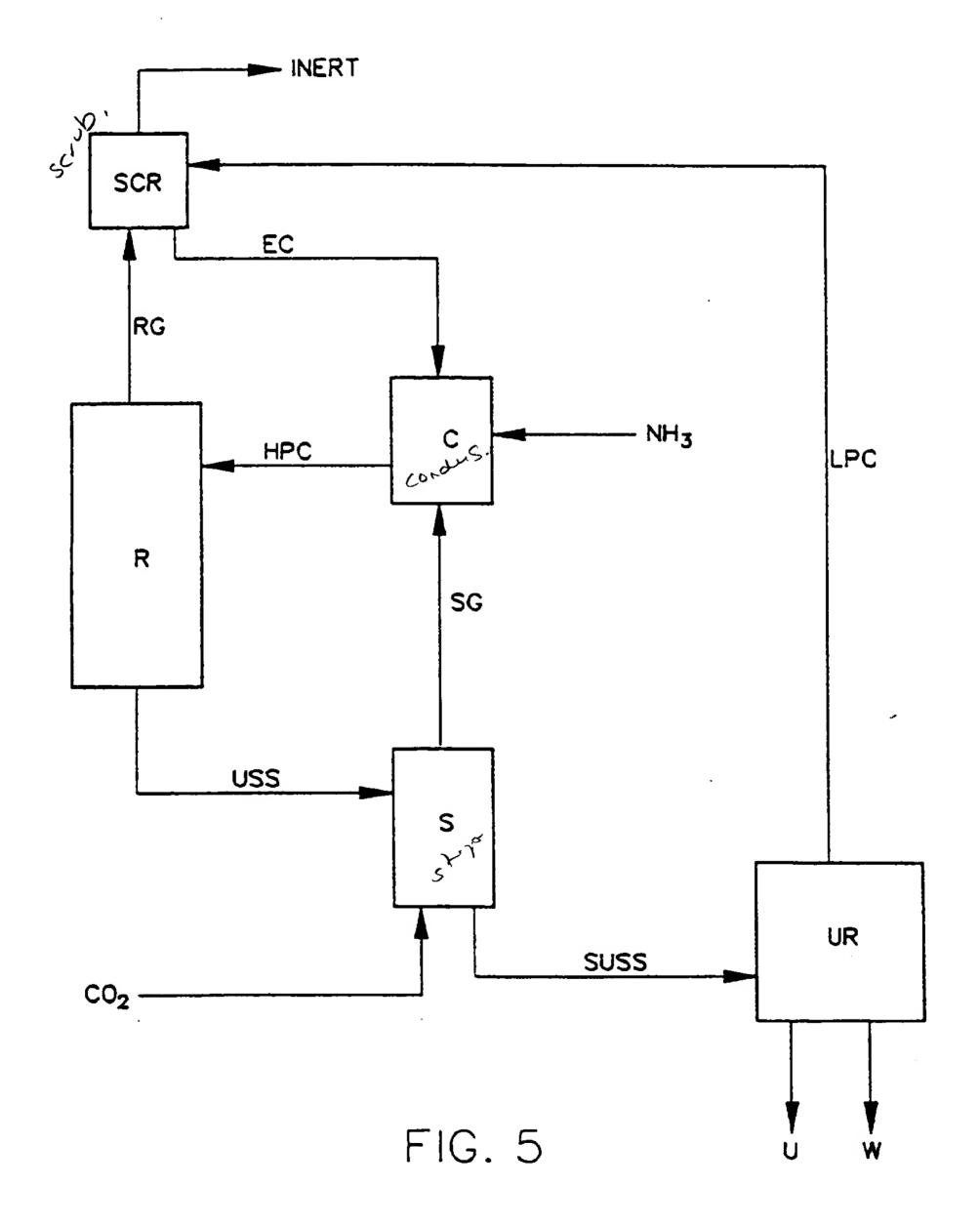
20

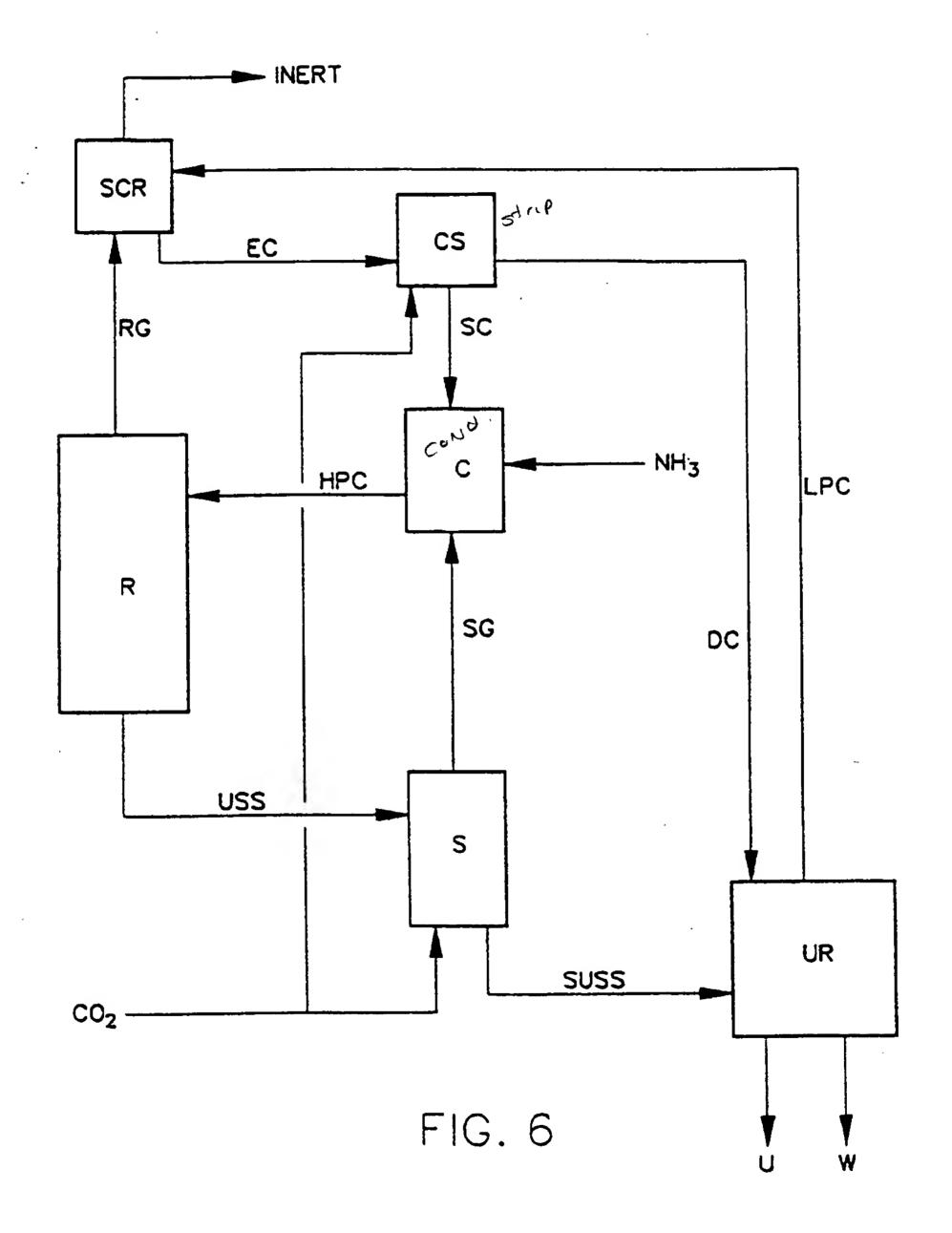
gas stream leaves the synthesis section, and using the low-pressure carbamate stream as a scrubbing liquid in it, after which the carbamate stream coming from the high-pressure scrubber are fed to CO<sub>2</sub>-carbamate stripper, after which this carbamate stream is stripped with CO<sub>2</sub> in this CO<sub>2</sub>-carbamate stripper, after which the carbamate gases that are virtually free of water are fed directly, or via a high-pressure carbamate condenser, to the synthesis section.

- 13. Method for improving and optimizing conventional urea plants by installing a CO<sub>2</sub>-carbamate stripper directly after the urea recovery, after which the gas stream from the CO<sub>2</sub>-carbamate stripper is condensed in an additionally installed high-pressure carbamate condenser.
- 14. Method for improving and optimizing an existing conventional urea plant by additionally installing a high-pressure scrubber, a CO<sub>2</sub>-carbamate stripper and a high-pressure carbamate condenser.









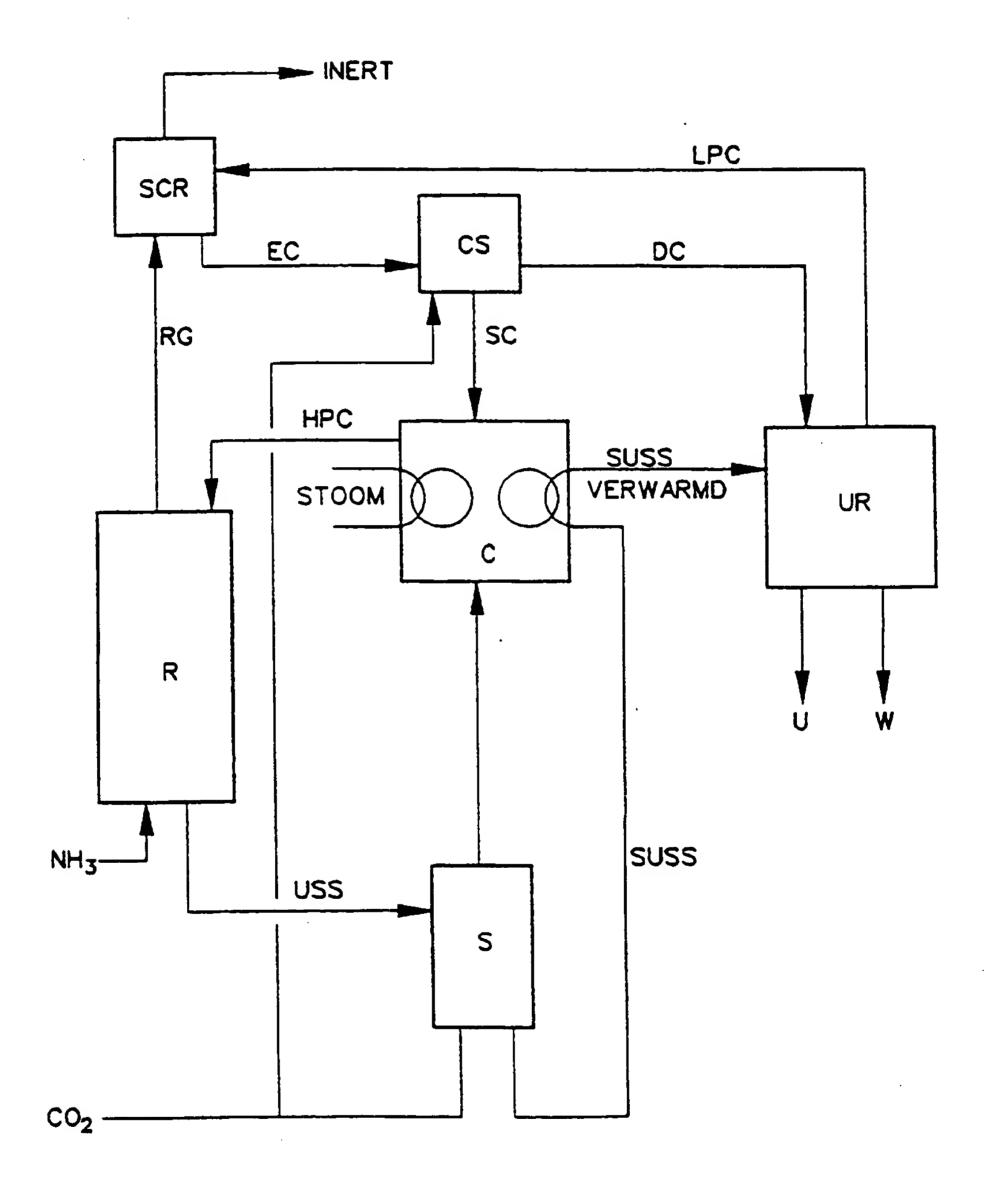
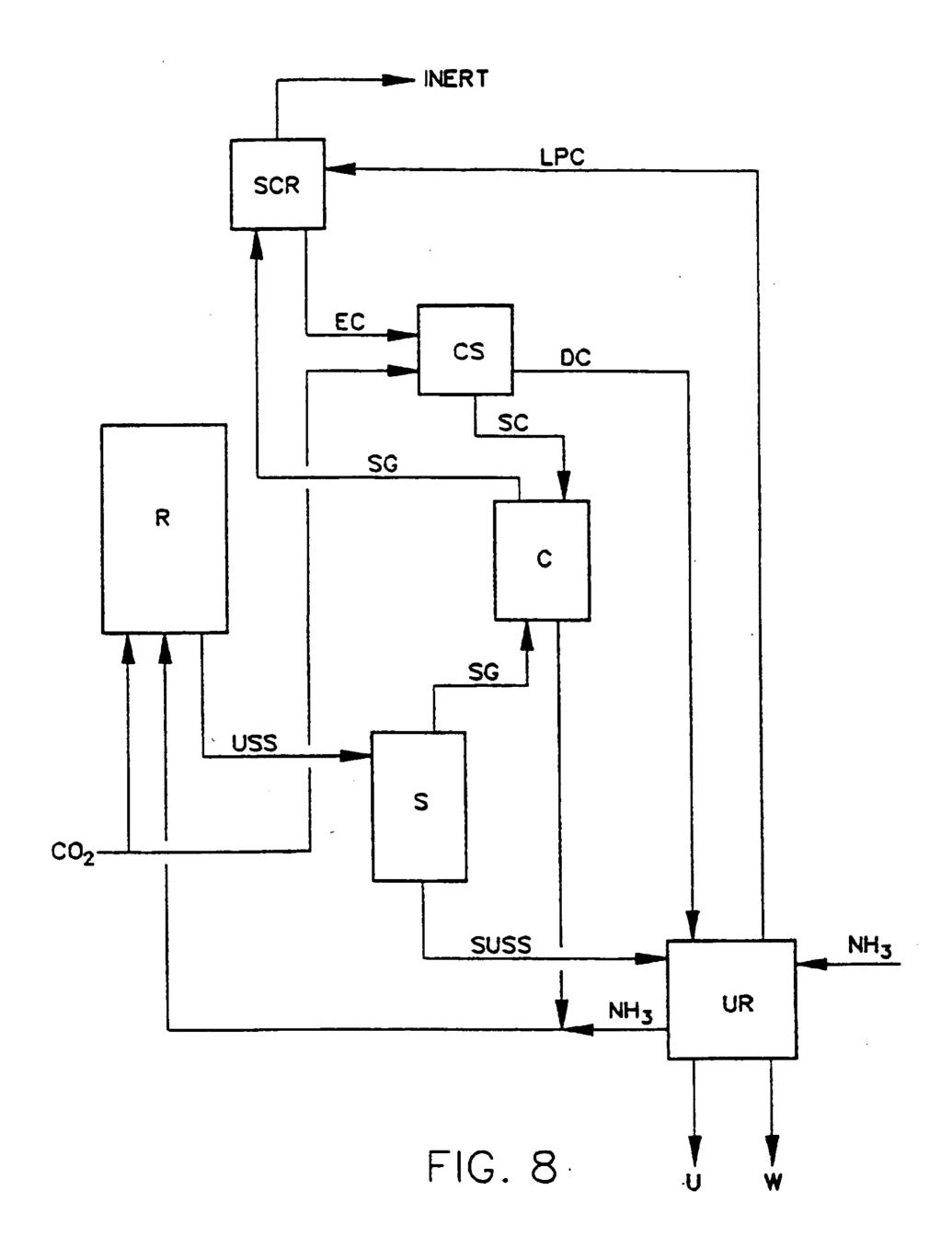


FIG. 7



## INTERNATIONAL SEARCH REPORT

Internal II Application No PCT/NL 98/00677

			1017112 3070077
	CO7C273/04		
According to	o international Patent Classification (IPC) or to both rudional class	uiteation and IPC	
B. FIELDS	SEARCHED		
	commentation see wheel (classification eyesem to fowed by classification eyes.	ication symbols)	
Documental	fon searched other than minimum documentation to the extent t	ud such documents are incl	uded in the links searched
Electronic d	ids. Lesse consulted during the international essuah (nerve of data	o basan medi, aftere predical	i, egarch toring used)
C. DOCUM	ENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the	e rolevert passages	Fieldvard to claim No.
A	US 4 613 696 A (U. ZARDI) 23 September 1986 see the whole document		1
A	EP 0 727 414 A (SNAMPROGETTI) 21 August 1996 cited in the application see claim 1		1
A	EP 0 611 753 A (UREA CASALE) 24 August 1994 see claim 1		1
Fur	ther documents are fished in the continuation of box C.	X Patent family	members on fished in soner.
'A' docum	ategories of cited documents : sent definite the general state of the surt which is not idened to be of particular relevance	or priority date as	blished after the international filing date nd not in conflict with the application but ad the principle or theory underlying the
"L" docum which cliatic	ment which may throw doubts on priority: claim(s) or h is clied to establish the publication date of another on or other special reason (se: specified)	cannot be coneid involve an invest these of memors "Y"	cultir felovence; the claimed invention dered novel or carnot be considered to the step when the document is falses alone cultir relevance; the claimed invention to act to involve an inventive about when the
"O" docum other "P" docum	nent referring to an ord disclosura, use, exhibition or reserve means.  The state of the international fling date tail then then the priority date calculated.	document is con reach, such con in the art.	bined with one or more other such docu- bination being obvious to a person skilled
<del></del>	actual completion of the international search		or of the earns patent family
	19 February 1999	26/02/	1999
Name and	mailing address; of the ISA European Potont Offico, P.B. 5816 Patentiaan 2 NL + 2200 HV Ribmilk	Authorized office	
	Tel. (+31-70) 340-2010, Tr. 31 651 epo ni. Fest: (+31-70) 340-3016	Englis	h, R

#### INTERNATI NAL SEARCH REPORT

inversation on patent femily members

PCT/NL 98/00677

Patent document ofted in search report	ì	Publication date		'stant tamily member(s)	Publication date
US 4613696	A	23-09-1986	CA	1329625 A	17-05-1994
			DE	3565532 A	17-11-1988
			EP	0180704 A	14-05-1986
			IN	164714 A	13-05-1989
		•	SU	1417794 A	15-08-1988
EP 0727414	A	21-08-1996	17	MI950281 A	16-08-1996
			CA	2168505 A	17-08-1996
			CN	1141913 A	05-02-1997
			JP	9020746 A	21-01-1997
			US	5763660 A	09-06-1998
EP 0611753	A	24-08-1994	CA	2113061 A	08-07-1994
			CH	1100717 A	29-03-1995
			ÜS	5684194 A	04-11-1997
			US	5681537 A	28-10-1997
			us	5792889 A	11-08-1998

Form PCT88AI210 (patent thereby memor) (July 1962)